Faculty of Resource Science and Technology

EFFECT OF REACTION TIME ON BASE HYDROLYSIS OF METHYL BENZOATE

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(43864)

Bachelor of Science with Honours
(Resource Chemistry)
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This project paper is submitted in partial fulfillment of requirements the Degree of Bachelor of Science with honors

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2016

Acknowledgement

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Table of Content

List of Abbreviation

C=O	Carbonyl
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
MeOH	Methanol
HCl	Hydrochloric Acid
KBr	Potassium Bromide

List of Table

List of Figure

Abstract

Hydrolysis is a reaction with water in general where the initially one compound converts to two compounds. Hydrolysis of methyl benzoate produced benzoic acid. Previous study found that the hydrolysis of *Jatropha curcas* seed oil to give free fatty acid (FFA) increase with increasing time. Therefore, this study aims to determine the effect of reaction time on base hydrolysis of methyl benzoate by using NaOH and KOH as catalyst. The effect of reaction time for base hydrolysis of benzoic acid by using NaOH and KOH as catalyst has been compared. Different reaction times (1.0, 2.0, 5.0, 7.0, 13.0 and 18.0) were used to determine the optimum yield in the presence and absence of methanol in base hydrolysis. The result obtained shown that percentage yield increase with increasing time.

Key Words: Base hydrolysis, Time, Benzoic acid, NaOH, KOH

Abstrak

Hidrolisis adalah tindak balas dengan air secara umum di mana satu kompaun pada mulanya menjadi dua sebatian. Hidrolisis methyl benzoate menghasilkan asid benzoik. Kajian sebelum ini mendapati bahawa hidrolisis minyak biji Jatropha curcas untuk menghasilkani asid lemak bebas (FFA) meningkat dengan peningkatan masa. Oleh itu, kajian ini bertujuan untuk menentukan kesan masa tindak balas pada hidrolisis methyl benzoate dengan menggunakan NaOH dan KOH sebagai pemangkin. Kesan masa tindak balas untuk hidrolisis alkali asid benzoik dengan menggunakan NaOH dan KOH sebagai pemangkin telah dibandingkan. Masa tindak balas yang berbeza (1.0, 2.0, 5.0, 7.0, 13.0 dan 18.0) telah digunakan untuk menentukan hasil optimum dengan kehadiran dan ketiadaan metanol dalam hidrolisis alkali. Keputusan yang diperolehi menunjukkan bahawa peningkatan hasil peratusan meningkat dengan peningkatan masa.

Kata kunci: Hidrolisis alkali, Masa, asid benzoik, NaOH, KOH

1.0 Introduction

1.1 Background

Methyl benzoate (Figure 1) is an ester that derived from benzoic acid (Marumaya *et al.*, 2012). It is a compound that has an ester group attached to a benzene ring. According to Marumaya *et al.* (2012), methyl benzoate plays an important role in the intermediate production of dyes, flavoring compounds, and mold growth biomarkers. The study found that methyl benzoate is important in the production of higher ester through transesterification in which methyl benzoate reacts with high boiling point alcohol such as butanol and benzyl alcohol to give benzyl or butyl benzoate and methanol as a product (Figure 2).

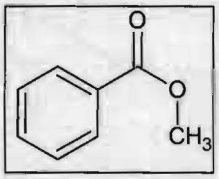

Figure 1: Structure of methyl benzoate

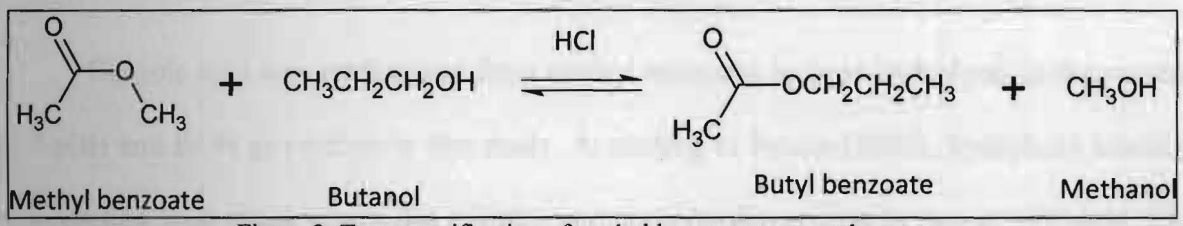

Figure 2: Transesterification of methyl benzoate to propyl acetate

Benzoic acid (Figure 3) is a compound that has a carboxylic group attached to a benzene ring. According to Bahl & Bahl (2006), benzoic acid is a white solid which is soluble in pure solvent with a melting point of 122°C and a boiling point of 249°C. The authors stated that benzoic acid is slightly soluble in cold water but dissolves completely in hot water. In addition, benzoic acid is important in various applications such as in medicines, food preservative and in dye industry. It is also used in cosmetic products (Nair, 2001). Benzoic acid can be prepared through various preparations such as oxidation of toluene, chlorinating of toluene followed by hydrolysis to give benzoic acid (Figure 4) and through reaction of phthalate anhydride in the presence of metal phthalate as catalyst (Bahl & Bahl,

2006). Benzoic acid should be handled carefully as the vapours could lead to the coughing and sneezing due to its pungent odor (Bahl & Bahl, 2006).

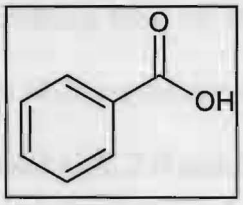

Figure 3: Structure of benzoic acid

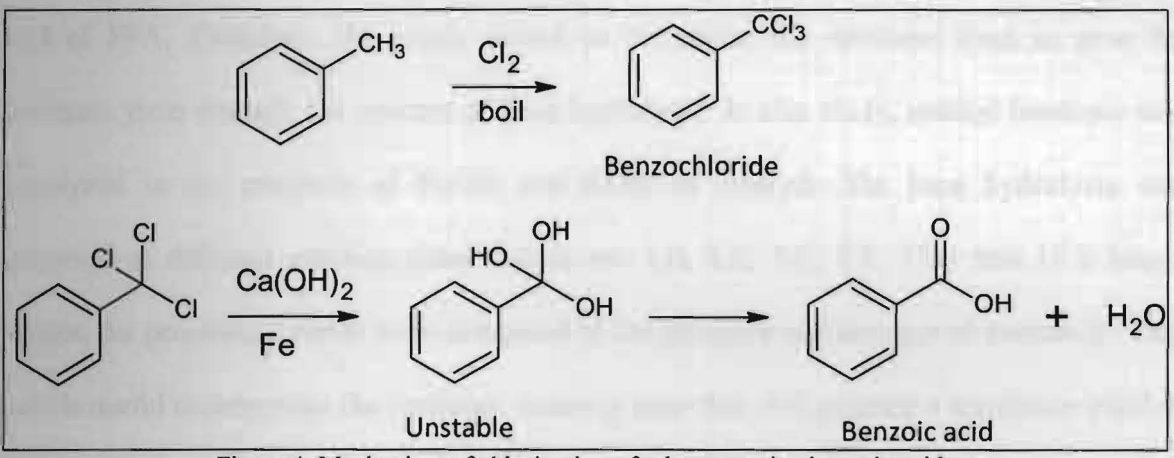

Figure 4: Mechanism of chlorinating of toluene to give benzoic acid

Benzoic acid was synthesized from methyl benzoate by base hydrolysis in the present of NaOH and KOH as catalyst in this study. According to Bruice (2006), hydrolysis reaction is a reaction with water where the initially one compound converts to two compounds. The study stated that ester was hydrolysed slowly because water is a poor nucleophile while the ester is a poor leaving group. However, the rate of reaction can be increased in the presence of acid or base as the catalyst. The one that used acid is known as acid hydrolysis while the one that used base is known as base hydrolysis. There are various organic compounds other than esters that undergo hydrolysis reaction such as amides, alkyl halides and epoxides (Al-Shamary *et al.*, 2014).

1.2 Problem statement

The study done by Al-Bahri *et al.* (2009) and Salimon *et al.* (2011) found that the percentage yield is increased with increasing time for the hydrolysis of ester. According to Salimon *et al.* (2011), in the hydrolysis of *Jatropha curcas* seed oil to produce free fatty acid (FFA) three different time have been used (1.5, 2.0 and 2.5 hours). The percentage of FFA is increase with time. Among these reaction times, 2.0 hours showed the highest percentage yield of FFA. Therefore, this study aimed to determine the optimum time to give the maximum yield through the process of base hydrolysis. In this study, methyl benzoate was hydrolyzed in the presence of NaOH and KOH as catalyst. The base hydrolysis was conducted at different reaction times which are 1.0, 2.0, 5.0, 7.0, 13.0 and 18.0 hours. Besides, the percentage yields were compared in the presence and absence of methanol. This study is useful to determine the optimum reaction time that will produce a maximum yield in hydrolysing the compound especially for ester group.

1.3 Objective

The main objective of this study is:

1. To determine the effect of reaction time on the base hydrolysis of methyl benzoate.
2. To compare the yield of hydrolysis in the presence and absence of methanol.
3. To analyze the hydrolysis product, benzoic acid by using NMR, FTIR and melting point analysis.

2.0 Literature Review

2.1 Ester

Many esters that are known today may either synthetic or natural. According to Ameen and Olatunji (2009), esters have been found in various applications such as in medicines, foods and preservatives. The study stated that one of the important esters; salicylates play a vital role in the food preservatives, pain control and fever control. Besides, acetyl salicylic acid (aspirin) is crucial in preventing the aggregation of platelets and stroke, an important analgesic and anti-inflammatory drugs. Sodium benzoate which is also the derivative of ester have been found to act as food preservative that inhibits microbial growth (Stanojevic *et al.*, 2009). The study done by Ameen and Olatunji (2009) found that the preparations of esters do have some limitation in which it involved lengthy work-ups and the products sometimes contain impurities. Thus, several modifications have been investigated for the preparation of esters in order to reduce the lengthy work-ups and increase the yields of products. One of the methods is by using sulphuric acids as catalyst to remove the water produced during the reaction.

2.1.1 Methyl benzoate

Methyl benzoate is one of the examples of carboxylic acid ester. The general formula for carboxylic acid ester is represented by $R_1C(=O)OR_2$ in which R_1 and R_2 can be alkyl chains, phenyl groups or heteroatoms. The reaction for the acid hydrolysis of carboxylic acid to form ester is the reversible of reaction of ester to form carboxylic acid (Bruice, 2006). It shows that methyl benzoate can be formed by benzoic acid. If ester is the desired product, the reaction should use an excess amount of alcohol in order to drive the reaction reversible. This process is known as Fischer's esterification (Figure 5). According to Francis (2003), methyl benzoate can react with ammonia to form amide. The study found that it is possible to carry

out the reaction in aqueous ammonia due to its higher ability as a nucleophile which is better than water (Figure 6).

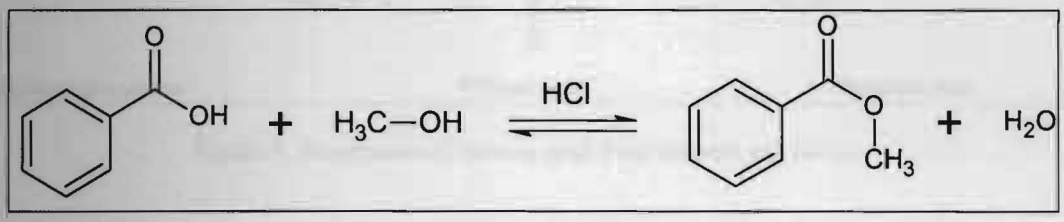

Figure 5: Fischer's esterification

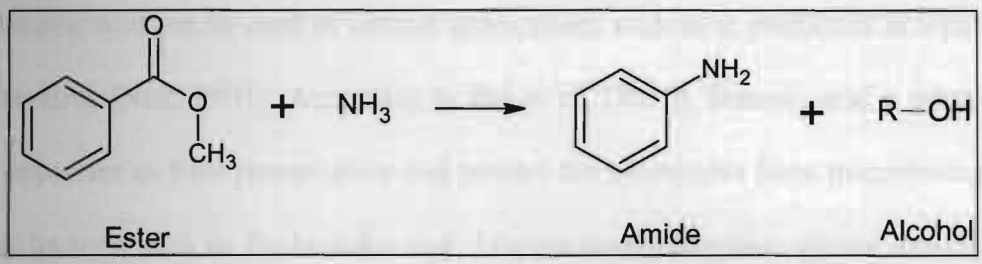

Figure 6: Reaction of methyl benzoate with ammonia

2.2 Benzoic acid

According to Bahl and Bahl (2006), benzoic acid was first discovered by Schlee (1775) from gum benzoin. The authors stated that benzoic acid is slightly soluble in cold water but dissolve completely in hot water. The study found that benzoic acid can be prepared in many general methods such as by oxidation of toluene with air in the presence of Co-Mn acetates as catalyst (Figure 7). Researchers also added that benzoic acid can be prepared by passing phthalic anhydride and steam over a metal phthalic catalyst at 200-300°C followed by decarboxylation of benzoic acid from the resulted phthalic acid (Figure 8).

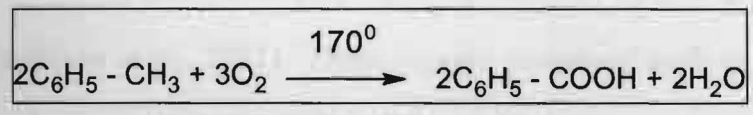

Figure 7: Oxidation of toluene with air

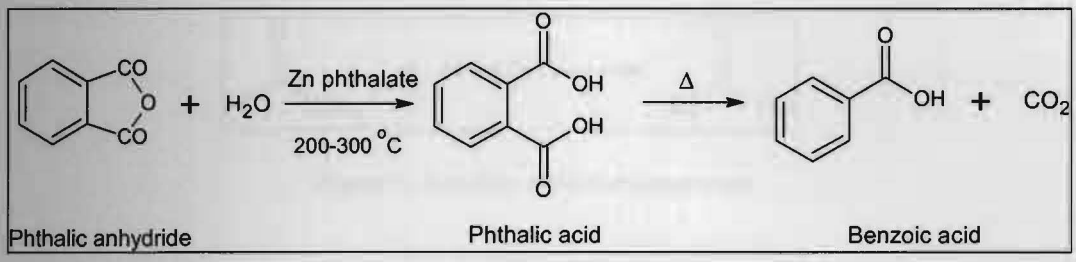

Figure 8: Preparation of benzoic acid from phthalic anhydride

2.1. Application of benzoic acid

Benzoic acid can be used in various applications such as in cosmetics as a pH adjuster d preservative (Nair, 2001). According to Rai *et al.* (2010), benzoic acid a group of food ditive important as food preservative and protect the consumers from microbiological risk various bacteria such as *Escherichia coli*, *Listeria monocytogenes*, genus *Aspergillus* and nus *Penicillium* which can cause food poisoning (Rai *et al.*, 2010). The study stated that dium benzoate which is less toxic is used mostly in acidic food such as salad dressings, rbonated drinks and jams due to it properties which are bacteriostatic and fungistatic under idic condition of pH below 4.0. According to Bahl and Bahl (2006), benzoic acid plays an portant role in medicine as urinary antiseptic and for disinfecting bronchial tubes in vapour m. It also can be used to make aniline blue in dye industry.

3 Hydrolysis

Hydrolysis is a chemical decomposition that involves the breaking of bond and the dition of water (Figure 9) (Ikhazuangbe & Oni, 2015). There are various applications that volved hydrolysis reaction such as hydrolysis of oils and fats to give glycerol and fatty ds (Figure 10) (Salimon *et al.*, 2011). Other organic compound such as carboxylic acid er, alkyl halide and epoxide also undergo hydrolysis in the medium of acidic, alkaline and utral (Al- Shamary *et al.*, 2014). Generally, process of hydrolysis is divided into two which base hydrolysis and acid hydrolysis (Kaye *et al.*, 2004).

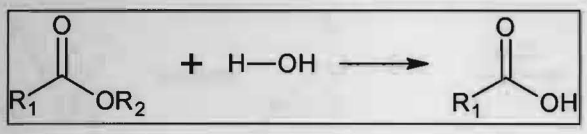

Figure 9: Equation of hydrolysis process

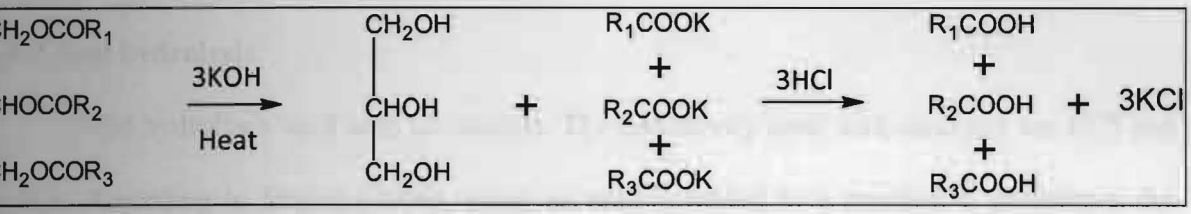

Figure 10: Hydrolysis reaction of oils and fats

.3.1 Base hydrolysis

Base hydrolysis is an irreversible process. It used base as a catalyst. The common ase that used in hydrolysis is NaOH and KOH. KOH based catalyst formulations have been eported to give better yields compared with NaOH based catalyst (Singh *et al.*, 2006). Due to s relationship with soap making, base catalyzed hydrolysis of ester is sometimes known as aponification (Salimon *et al.*, 2011). There are two advantages of doing base hydrolysis. irst, it is a one way reaction and next, the product is easier to separate (Salimon *et al.*, 2011). ccording to a previous study, it has been found that the percentage yield is increase with the ncreasing time (Salimon *et al.*, 2011). The increasing concentration of catalyst and increase reaction temperature also increase the productions yield in hydrolysis (Singh *et al.*, 2006).

.3.2 Base hydrolysis of carboxylic ester

According to Al-Shamary *et al.* (2014), base hydrolysis of carboxylic ester generally kes place via S_N2 reaction in which the hydroxide ion attacks the carbonyl carbon of an ster to give carboxylic acid and an alcohol (Figure 11). Moreover, the presence of water as olvent and other organic solvent could alter the hydrolytic rate and modify the mechanism of ydrolysis reaction in various ways such as nucleophilic reagent, as a high dielectric constant nd as a specific solvating agent for organic reactant and product.

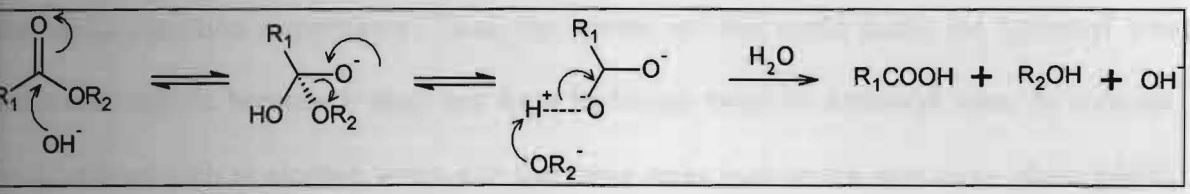

Figure 11: Mechanism of base hydrolysis of carboxylic ester

2.3.2 Acid hydrolysis

Acid hydrolysis used acid as catalyst. The commonly used acid catalysts are HCl and H_2SO_4. According to Bruice (2006), when an acid is added to a reaction it protonates the atom in the reactant that has the greatest electron density which is the carbonyl group in ester. Thus, it increases the rate of reaction in tetrahedral intermediate by protonating the carbonyl group. The protonated carbonyl group is more susceptible to nucleophilic attacks compared with non-protonated carbonyl due to the positive charge that is more electrons withdrawing. As a result, it reduces the basicity of the leaving group which makes it easier to eliminate.

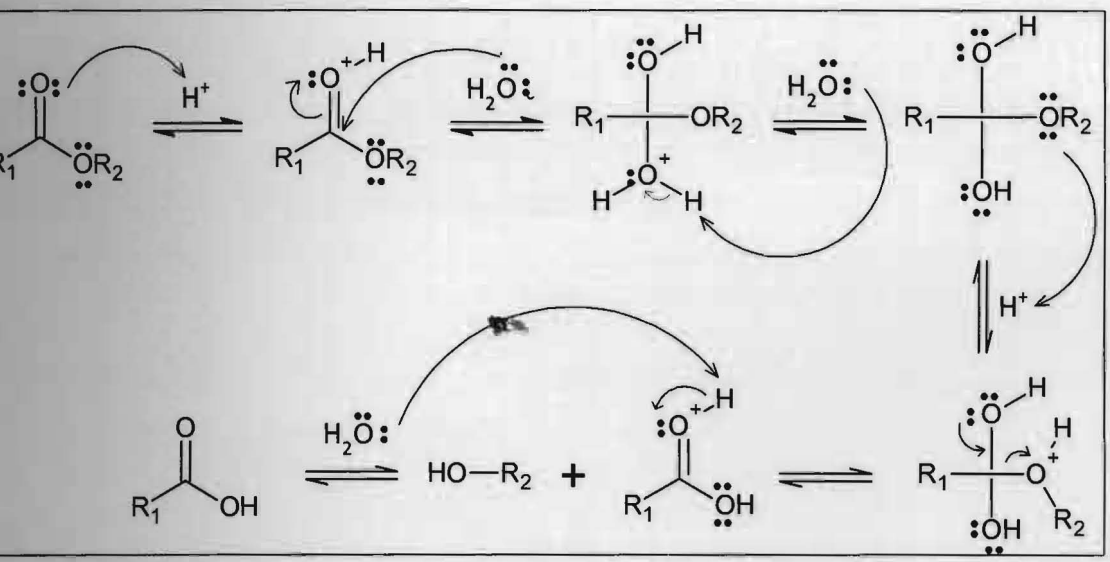

Figure 12: Mechanism of acid hydrolysis

2.3.3 Solvent effects on hydrolysis

As mentioned by Brinker (1988), solvent molecules that formed hydrogen bond to hydroxyl or hydronium ions catalyzed in hydrolysis reduce the catalytic activity under basic

and acidic condition respectively. Thus, the aprotic solvent could make the hydroxyl ions more nucleophilic because it does not form hydrogen bond to hydroxyl ions. In contrast, protic solvent such as alcohol, water and ammonia make hydronium ions more electrophilic. Thus, the presence of MeOH in this study can act as donors and acceptors in hydrogen bonding. The used of organic solvent give several advantages which are increased activity and stability, regiospecificity and stereoselectivity and ease of products recovery (Sharma and Kanwar, 2014).

3.0 Materials and Methods

3.1 Preparation of 2 M NaOH

80 g of NaOH pellet were weighed by using an electronic balance. The pellets were placed in 500 mL of volumetric flask and distilled water was added to it. After the solution was cooled down, distilled water was added to the volumetric flask again until it reached the mark level.

3.2 Preparation of 2 M KOH

56.11 g of KOH pellet were weighed by using electronic balance. The pellets were placed in 500 mL of volumetric flask and distilled water was added to it. After the solution was cooled down, distilled water was added to the volumetric flask again until it reached the mark level.

3.3 Preparation of 2 M HCl

Distilled water was added to a 200 mL beaker followed by 33 mL of HCl. After the solution cooled down, distilled water was added to the beaker until it reached 200 mL.

3.4 Base hydrolysis of methyl benzoate with solvent

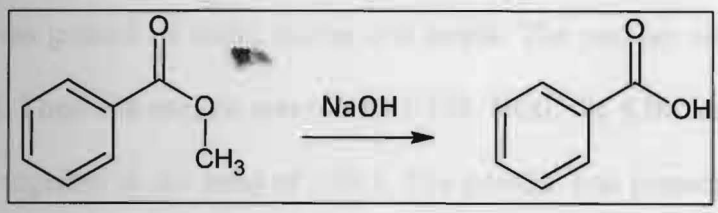

Figure 13: Pathway of hydrolysis of benzoic acid from methyl benzoate

Methyl benzoate (2 mL, 0.02 mol) was added to a 250 mL round bottomed flask and a stirrer bar was placed inside the flask. MeOH (2 mL) was added to the flask and the mixture was stirred until the mixture was homogenous. Next, NaOH/KOH (30mL) was added and the mixture was stirred for 2 hours. After 2 hours, HCl (50 mL) was poured into the mixture